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A calorimetric and resistometric study on the transformations in AuCu

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With 7 figures in the text

§ 1. Introduction

One of the best known order-disorder transformations in alloys is that of the gold-copper alloy AuCu. In 1916 KURNAKOW, ZEMCZUZNY and ZASEDATELEV (1) found that there is a transition in the alloy at about 400° C, and JOHANSSON and LINDE (2) showed that this was an order-disorder transformation.

Later the alloy has been studied by means of measurements of the electrical resistance by BORELIUS, JOHANSSON and LINDE (3), by means of X-rays by GORSKY (4, 5), JOHANSSON and LINDE (6), HULTGREN and TARNOPOL (7), KÄLLBÄCK, NYSTRÖM and BORELIUS (8), HARKER (9).

The first theoretical investigations on order-disorder transformations were made by GORSKY (4), BORELIUS (10), BRAGG and WILLIAMS (11, 12) and BETHE (13). In most of the theories the internal energy of the alloy is assumed to be determined by the binding energy between pairs of nearest neighbours of atoms, but this approximation does not seem to be suitable for the experimentally investigated alloys (14). BORELIUS (10) has specialized his calculations to an alloy of the stoichiometric composition AB, but the energy of the alloy is assumed to be determined not only by pairs but also by larger groups of atoms, for instance 3 or 4. In this way it has been possible to obtain good agreement with experimentally investigated alloys. Using the developed formulae, he has calculated the evolution of heat during the order-disorder transformation in AuCu from the kinetic results obtained in (8). During the last two years attempts have been made by BORELIUS and co-workers to measure the evolution of heat during this transition (15), and this investigation, which is confined to rapid transformations, is one of these attempts. The other experimental work and a discussion of the calorimetric results will be published at the same time as this work (16).

§ 2. Experimental arrangements

The alloy was made of pure gold from Ädelmetallbolaget in Malmö, and copper with especially low electrical resistance, obtained from Sieverts Kabelverk in Stockholm. The metals were weighed with an accuracy of about ±0.1 mg, and the total weight of the alloy was about 5 g. The alloy was molten in an evacuated silica tube

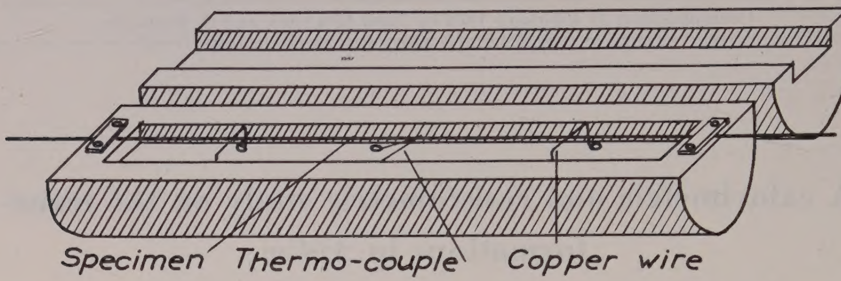

Fig. 1. Apparatus for the calorimetric and resistance measurements.

in a high frequency furnace, and the loss in weight was about 3 mg. As it is impossible to work the alloy in the ordered state, it had to be quenched very effectively from a temperature above the critical. So the alloy was annealed at 500° C in an evacuated glass tube for half an hour and quenched by dropping the tube directly into cold water. Thereupon the alloy was rolled a little and homogenized about 30° below the solidus point for 15 hours in a silica tube. Finally it was again heated in a glass tube and quenched in cold water. After this treatment the alloy ought to be homogeneous and it was possible to roll and draw a wire about 0.6 mm in diameter from it.

The specimen wire was mounted almost in the same way as has been described in a previous investigation on the evolution of heat during precipitation in lead-tin alloys (17). The specimen was fixed on a copper block (Fig. 1) and two crossing wires were spotwelded to the specimen. A few millimetres of these wires in the neighbourhood of the specimen were of the alloy, and the other parts of copper. The thermo-couples were fastened to the specimen by means of silicon varnish as previously. For some of the measurements the thermo-couples were made of constantan and manganin, for others of two gold alloys with 7 atomic percent nickel and 1 atomic percent titanium respectively. A thermo-couple made of these alloys, which had kindly been put at my disposal by Dr. LINDE, had an e.m.f. of about 50 μV/degree at room temperature. In some cases only a single thermo-couple was used as the evolution of heat was very large during the transition and in many cases also rapid. During the most rapid transformations the temperature of the specimen increased about 30° C above that of the copper block.

To prevent oxidation of the apparatus and the specimen, they were enclosed in a pyrex glass tube filled with a mixture of 95 % nitrogen and 5 % hydrogen to a pressure a little higher than that of the atmosphere outside. The silicon varnish, which can be used at 250° C in air, was not spoiled even at 450° C in this gas mixture. The wires for the electrical connections were drawn through a rubber stopper. In spite of this, the apparatus was so tight that it was not necessary to fill it with gas more than two or three times a week.

To determine the evolution of heat during the slow transformations it was necessary to have the temperature very constant, but for the rapid transformations this was not so. The apparatus was heated in a furnace with a large heat capacity by means of a stabilized electric current. The same heating arrangements had been used earlier by WICTORIN (18). In this way it was possible to have a constant temperature in the neighbourhood of 400° C with an accuracy of about 0.1 degree for several hours.

§ 3. The calorimetric measurements

The determination of the evolution of heat during the transition was made in the same way as in the investigation of the lead-tin alloys (17). To transform the specimen into the disordered state, electric currents were sent through it and the crossing copper wires. A special control was made to see if a sufficiently long part of the specimen was heated above the critical point, 408° C. An extra thermo-couple was fixed to one of the contact points between the specimen and the copper wires by means of silicon varnish, and the temperature was read during the annealing. If the currents were sufficiently high, the temperature of the thermo-couple increased rapidly to about 420° C. Then the specimen was transformed into the disordered state at an almost constant temperature with an accompanying absorbtion of heat. After about one minute the temperature increased very rapidly again when the transition had been completed. The temperature rose several tens of degrees since the resistance of the alloy was much higher in the disordered than in the ordered state, and the current was almost independent of the resistance of the alloy. As shown by

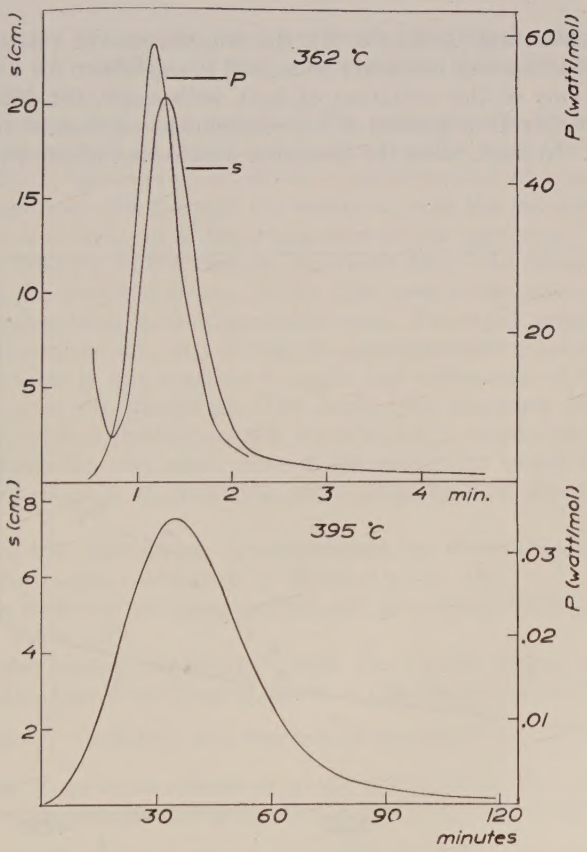

Fig. 2. Galvanometer deflection s and heat per second P as a function of time.

Table 1

Total amount of heat evolved (U) at different temperatures.

t (°C)	U (joule/mol)	t (°C)	U (joule/mol)
334	2920	379	1840
341	2900	380	1950
352	3080	383	1870
361	2775	386	1835
362	2605	391	1685
366	2490	393	1695
368	2450	394	1740
369	2185	395	1620
371	2390	397	1660
375	2170	400	1760

Källbäck, Nyström and Borelius (8), the transformation velocity is very high above 420° C, and it was not necessary to anneal the specimen for a long time there. Some determinations of the evolution of heat were made for different annealing times, but the heat evolved seemed to be independent of them if they were longer than one minute. In most cases the specimen was heated about two minutes. For

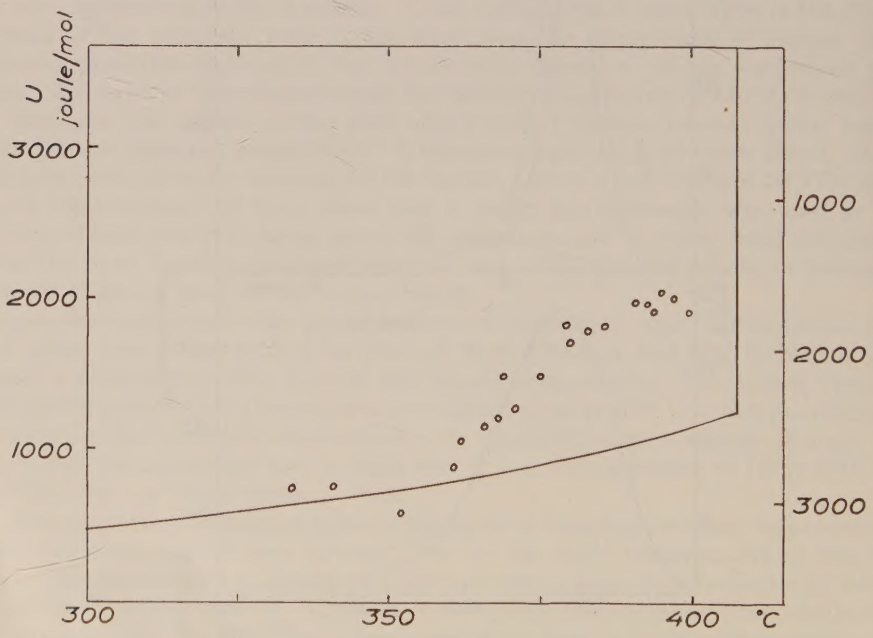

Fig. 3. Evolution of heat during the order-disorder transition in AuCu.

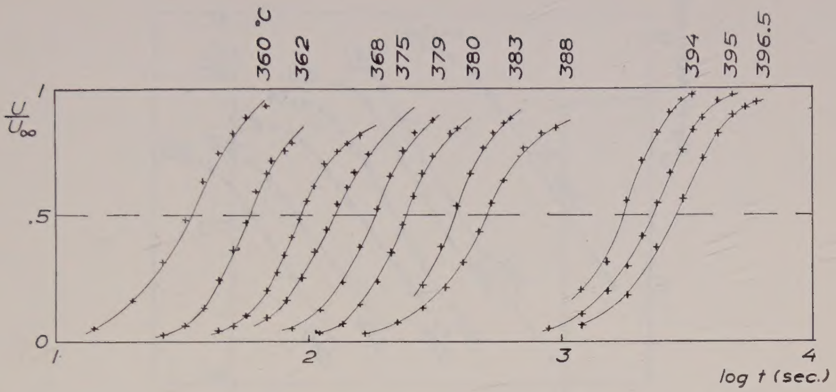

Fig. 4. $\frac{U}{U_\infty}$ against logarithm of time.

long annealing times the copper block was heated too much, and a correction had to be made when the evolution of heat was calculated from the e.m.f. of the thermo-couples, as shown previously (17).

When the specimen had been annealed, the currents were broken and the e.m.f. of the thermo-couples read on a galvanometer or recorded as in the previous investigation (17). In Fig. 2 two curves are shown of the evolution of heat. For calibration an electric current was sent through the specimen, and the galvanometer deflection was determined as a function of the Joule heat in the specimen. The deflection is, however, also a function of the thermal conductivity of the specimen, which is not constant during the transformation. If the alloy was in the ordered state, the conductivity was higher than in the disordered state. For rapid transformations it was impossible to investigate this, but during the measurements on slow transformations at high temperatures it was possible to make one calibration of the thermo-couple before and one after the transition. The Joule heat necessary for a certain e.m.f. of the thermo-couples in the former case was about 5 % smaller than after the transition. To determine the true mean value of the sensitivity would be rather difficult, but the variation is only of about the same magnitude as the uncertainty of the measurements.

The results of the calorimetric measurements are shown in Table 1 and Fig. 3 together with the values calculated by Borelius (15, 16).

The difference between the experimental and calculated values is discussed in the latter of these works (16).

To compare the kinetic results in (8) with the kinetic results of the calorimetric measurements, the heat U evolved at the time t is divided by the total heat evolved U_∞, and the ratio $\frac{U}{U_\infty}$ is plotted as a function of the logarithm of the time t in diagram 4. This diagram is quite analogous to those from which the half-value times are calculated from the measurements on the X-ray lines. The logarithm of the half-value time for which $\frac{U}{U_\infty} = \frac{1}{2}$ is then plotted in diagram 7 together with the results

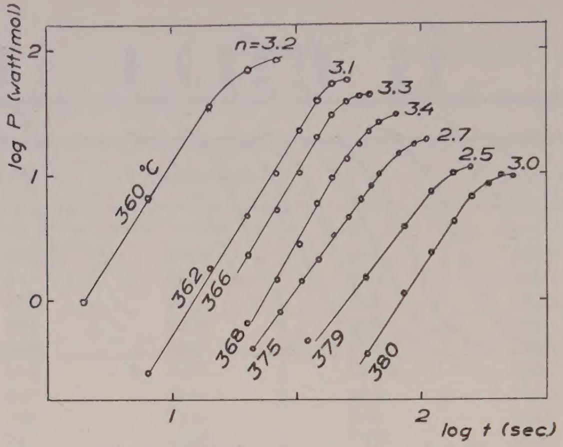

Fig. 5. Logarithm of heat per second against logarithm of time to determine n in the formula $P = \text{const} \times t^n$.

of the other kinetic measurements. As seen from the figure they are in good agreement with the X-ray measurements.

From curves like those in Fig. 2 the logarithm of the heat per second was calculated and plotted as a function of the logarithm of time (Fig. 5). The heat per second is seen to increase as the third power of the time. This is discussed elsewhere (16).

§ 4. The resistance measurements

Like Borelius, Johansson and Linde (3), the author found during the calorimetric measurements that the electric resistance was different for different treatments of the specimen in the neighbourhood of 380° C. Previously two different ordered states of the alloy were known; one with a tetragonal lattice, which has been called AuCu I, and the other with an orthorhombic structure AuCu II (6). As shown by Källbäck, Nyström and Borelius (8), AuCu II is obtained by annealing the disordered form above 380° C and AuCu I by annealing it below this temperature. In the present investigation it was found that the specimen obtained a higher electric resistance above than below 380° C if it had been annealed at a higher temperature than the critical point, 408° C. From these facts it was concluded that AuCu II has a higher resistance than AuCu I.

In Fig. 6 the resistance of one specimen as a function of the temperature is shown. The fully drawn lines indicate that the corresponding state of the alloy is stable. The dotted lines indicate metastable states. If the thermal expansion from room temperature is neglected, the resistivity of the disordered state at 408° C is 16.9×10^{-6} ohm cm, and that of AuCu I and AuCu II at 380° C 9.8×10^{-6} ohm cm and 11.6×10^{-6} ohm cm.

To explain the results of the measurements of the resistance by Borelius, Johansson and Linde, a kinetic investigation of the transitions between AuCu I and AuCu II was made. The specimen was held sufficiently long at a constant temperature below or above 380° C for the resistance to become constant.

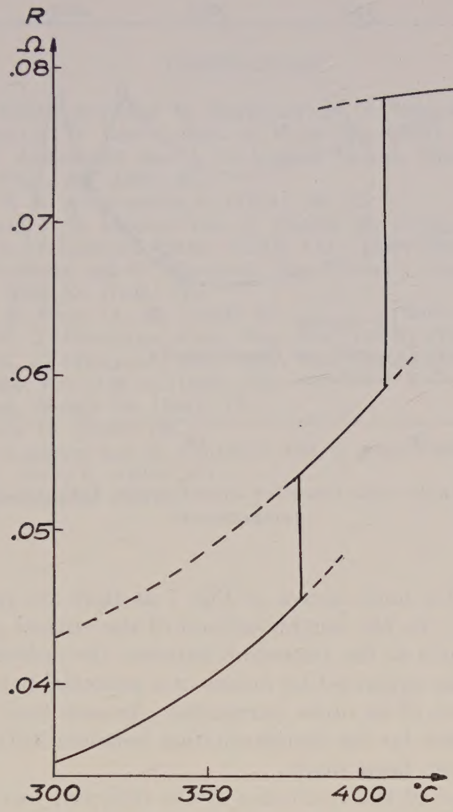

Fig. 6. Electrical resistance of a specimen as a function of temperature.

Then the furnace was brought as rapidly as possible to a distinct point on the other side of this temperature, and the resistance was measured as a function of time. Usually the transformation had already begun before the measuring temperature was reached, but in most cases it was possible to obtain an approximate half-value time for the change of resistance from the velocity of the variation of the resistance.

The logarithms of the half-value times are plotted in Fig. 7 as a function of the inverse absolute temperature together with the kinetic results of Källbäck, Nyström and Borelius. It is interesting to see that the form of the two curves is the same, but the transformation velocity between AuCu I and AuCu II is smaller than that between the disordered and the ordered states.

As pointed out by Källbäck, Nyström and Borelius, the rate of the disorder-order transition is determined at low temperatures by the diffusion; consequently it may be written as a constant times $e^{-\frac{Q}{RT}}$ where Q is the diffusion energy per mol, R the gas constant, and T the absolute temperature. This means that the logarithm of the half-value time is a linear function of $\frac{1}{T}$ as seen from the figure. The constant Q

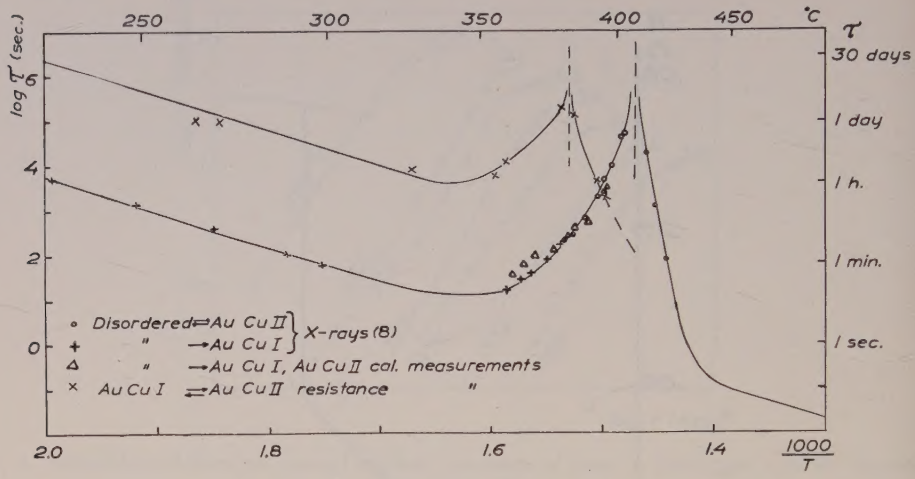

Fig. 7. Logarithm of half-value times for transitions in AuCu against inverse absolute temperature.

seems to be the same for both curves in Fig. 7 as they are parallel within the experimental uncertainty. In the neighbourhood of the critical point 408° C, there is, however, another obstacle to the transition between the ordered and the disordered state, which Borelius has explained by means of a potential barrier in the diagram of free energy as a function of an order parameter. As seen from the diagram there is something of this nature for the transformation between AuCu I and AuCu II, but no calculations have yet been made.

Concerning the value of the resistance of the different forms of AuCu, it is well known that ordered states of alloys have a lower resistance than the disordered. The resistance of AuCu II is higher than that of AuCu I. As the lattice of AuCu II is very like that of AuCu I, the higher resistance may be explained by the fact that the AuCu II lattice can be obtained from AuCu I if small domains, with a size of ten atomic distances are displaced one atomic distance in relation to each other. The surfaces of the displacements are then assumed to interfere with the electronic waves in the alloy. For a theoretical investigation of this, however, further experimental information from resistance measurements on single crystals of AuCu I and AuCu II may be necessary.

This investigation has been carried out at the Physical Department of the Royal Institute of Technology in Stockholm. To the Director of the Department, Professor G. Borelius, who suggested the work, I beg to express my gratitude for valuable discussion and good advice.

Further I wish to thank Dr. J. O. Linde for discussions and valuable information about earlier work on AuCu.

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